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THE ELECTRICAL SWITCHING PROPERTIES OF AMORPHOUS BISMUTH TRIOXI--ETC(U)
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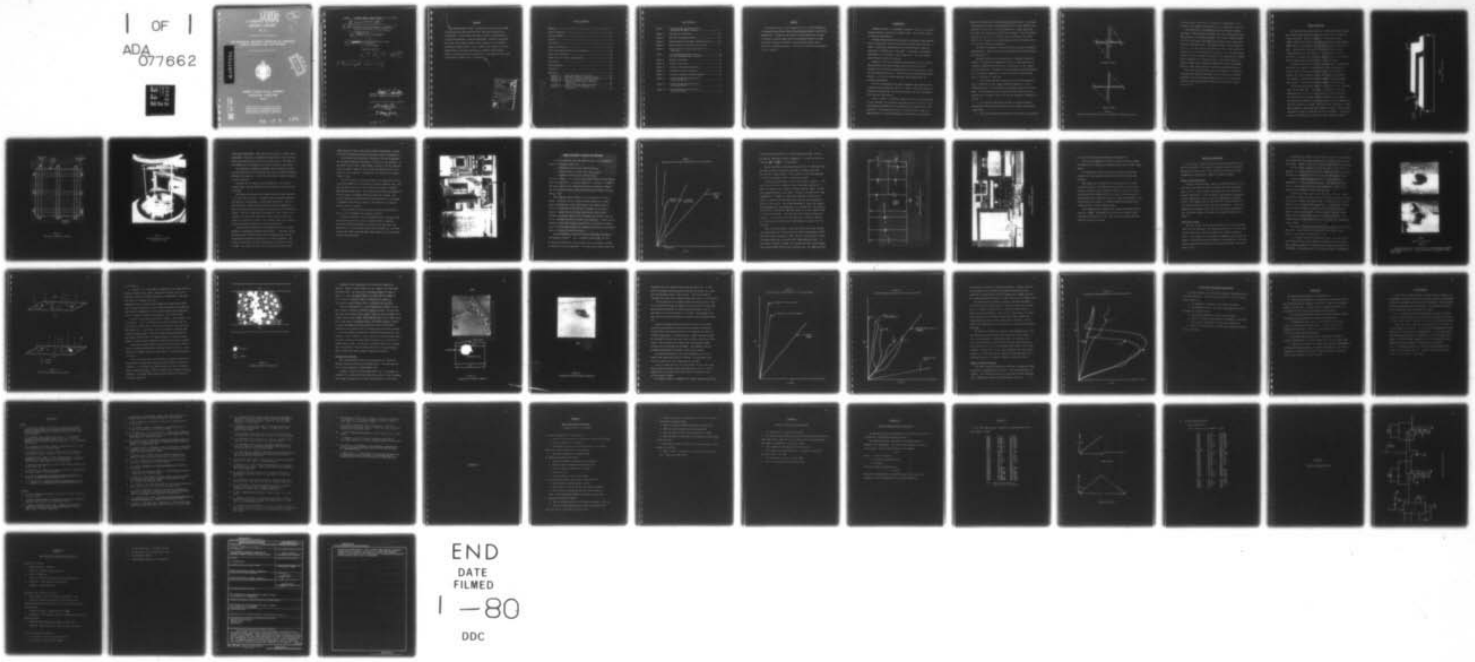

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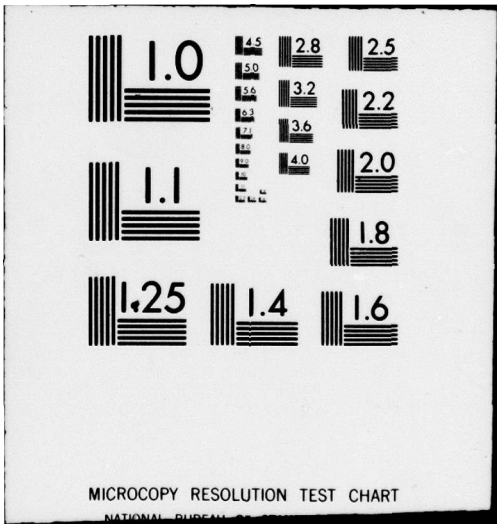
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BISMUTH TRIOXIDE THIN FILM DEVICES

UNITED STATES NAVAL ACADEMY
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(6) "The Electrical Switching Properties of Amorphous Bismuth Trioxide Thin Film Devices"

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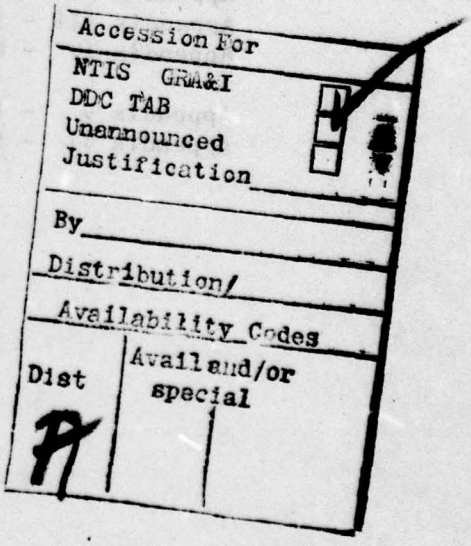
ABSTRACT

Many gold-amorphous bismuth trioxide-gold layered devices, known as Bi-O-Trons were fabricated and their switching properties were investigated. The Bi-O-Trons were made by direct vacuum deposition. A unique microprocessor controlled measurement method was developed. This report also contains evidence that filaments can be formed by exclusively thermal effects. Also, evidence that suggests an electro-thermal model of threshold switching is presented and discussed. Finally a conclusion about the possibility of the immediate application of Bi-O-Trons as memory cells is presented.



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PREFACE

The original title of this research was to be "The Development of a Programmable Read-Mostly Memory Using Amorphous Bismuth Trioxide Thin Film Devices." During the past year it became evident that in order to develop a reliable memory device from amorphous bismuth trioxide thin films it would be necessary to learn much more about their electrical switching properties. The new title reflects this change of research emphasis.

INTRODUCTION

Bismuth trioxide is a polymorphic substance. That is, it can exist in many different structures or physical forms. One of these forms is an amorphous semiconductor.

Amorphous semiconductors differ from the crystalline semiconductors used in conventional solid state electronic devices such as the transistor. Crystalline semiconductors are characterized by a specific order that is repeated over a long range. In contrast, the amorphous semiconductor only possesses a short range order. They also exhibit much different electrical properties.

Research in the area of amorphous semiconductors is very exciting. These materials have displayed many properties that are not well explained with the present understanding of solid state physics. Also, they have many potential uses. Some of the more promising applications include: non-volatile computer memories, photocopying paper and silverless photography.

The first investigators who studied amorphous semiconductors were a group of Soviet physicists led by A. F. Ioffe. They found them to be relatively uninteresting. But this was because they only investigated "low" electric field effects.

Later, in 1958, S. R. Ovshinsky began his work with these materials in Troy, Michigan. He found that upon application of an electric pulse his amorphous semiconductor (a chalcogenide glass) changed from a high resistivity, low conductivity state to a low resistivity, high conductivity state. He also discovered that the process was reversible.

News of his results spread quickly and many others began to investigate the reversible electrical switching properties of other amorphous semiconductors. Since then it has been observed in: Nb_2O_5, $A\ell_2O_3$, VO_2, NiO, TiO_2, CuO, Fe_2O_3, GaAs, Cr_2O_3, SiO_2 and Bi_2O_3.[1] The investigation of Bi_2O_3 was done by J. H. Halford at Duke University in the early 1970's. It is because of his pioneering work with this material that this research project was undertaken.

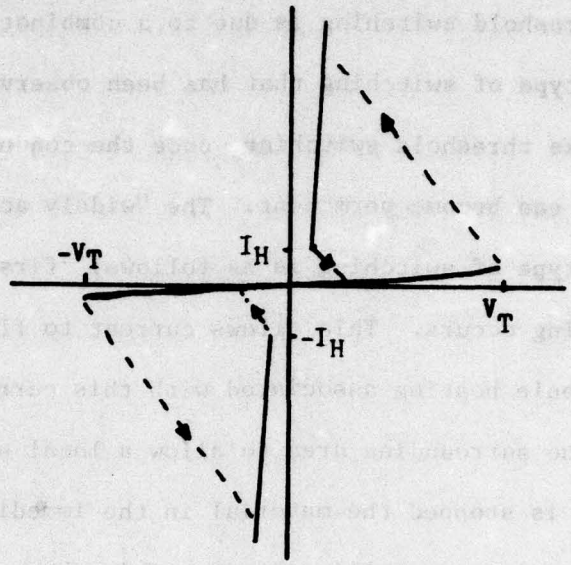
Two types of reversible switching have been observed in amorphous semiconductors. They are known as (1) threshold and (2) memory switching (See Figure 1.).

Threshold switching is characterized by a "holding" current and voltage. This means that whenever the electrical switching pulse is completely removed from the material it reverts back to its original non-conducting state. The physics of the threshold switching mechanism is not completely understood. There are basically three proposed models to explain it. They are:

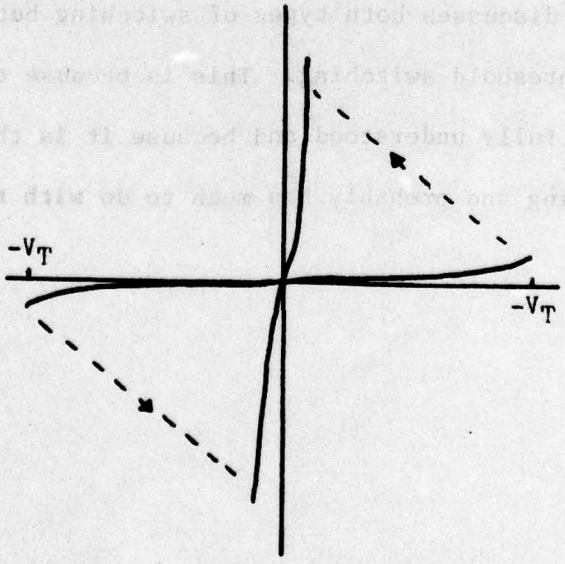
1. The thermal model which proposes that threshold switching is due to "formation of a hot, highly conducting channel in a cool, resistive matrix."[2] These channels are sometimes referred to as filaments. This explanation only involves macroscopic qualities of the material such as thermal conductivity and the temperature dependence of current.

2. The electronic model which attempts to explain threshold switching with only microscopic effects such as charge injection and charge traps.

3. The electro-thermal model maintains that neither the electronic



Threshold Switch



Memory Switch

Figure 1

Current-Voltage Characteristics of Threshold and Memory Switches

or thermal model is sufficient to explain all observations. So it proposes that threshold switching is due to a combination of the two.

The second type of switching that has been observed is memory switching. Unlike threshold switching, once the conducting state has been achieved it can become permanent. The "widely accepted explanation"[3] for this type of switching is as follows: first, some type of threshold switching occurs. This allows current to flow through the material. The joule heating associated with this current raises the temperature of the surrounding area to allow a local structure change. When the current is stopped the material in the immediate area changes from an amorphous to a crystalline state. This phase change also causes a change in the electrical conductivity because an amorphous material cannot conduct electricity but the crystalline state can.

This report discusses both types of switching but is primarily concerned with threshold switching. This is because the threshold mechanism is not fully understood and because it is the first step in memory switching and probably has much to do with the latter's unreliability.

SAMPLE PREPARATION

The reversible switching properties of amorphous bismuth trioxide were studied using Au-Bi_2O_3-Au sandwich structure thin film devices called Bi-O-Trons. Each one consists of a thin layer of gold (250Å to 750Å thick) followed by a layer of bismuth trioxide (300Å to 5000Å thick) in the amorphous form and finally another thin layer of gold. Conditions were arranged so that nine of them were made simultaneously on the same substrate. (See Figures 2 and 3.) A Bi-O-Tron is formed as can be seen in Figures 2 and 3, at each point where an upper gold strip passes over a lower gold strip.

The devices were made by direct vacuum deposition. This method was found to be superior to other methods, such as oxidation of bismuth films, reactive sputtering and surface film formation.[1] However, the direct deposition process did present some problems. For instance, it was found that molten bismuth trioxide destroyed most sources.[1] The only source not attacked by it was platinum.

The sources were mounted parallel to each other at the approximate center of the base plate. (See Figure 4.) Bismuth trioxide was evaporated from a 7.2 cm x 3.0 cm platinum foil boat containing a 0.5 cm deep by 2.0 cm diameter circular depression in the middle. The boat used to evaporate the gold was alumina coated molybdenum that was 10 cm long and 1.7 cm wide. The sources were connected to a power supply capable of delivering three kilowatts of power. Pattern masks were made according to the method outlined in Appendix I. These were mounted on stainless steel plates which were rotatable by means of

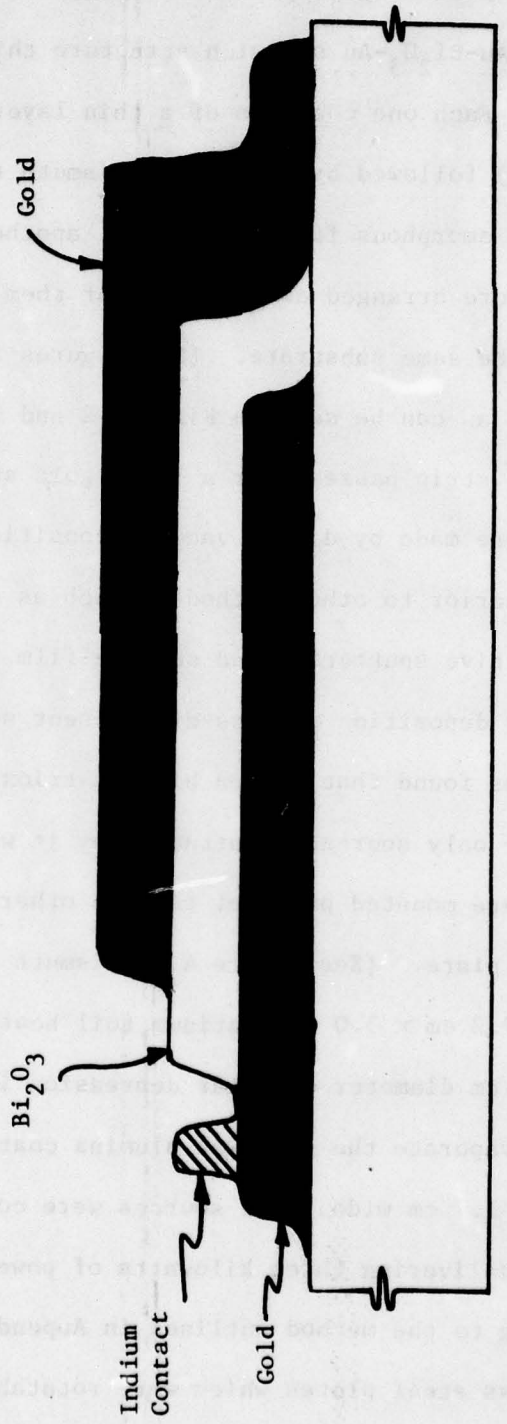


Figure 2
Side View of a Bi-O-Tron

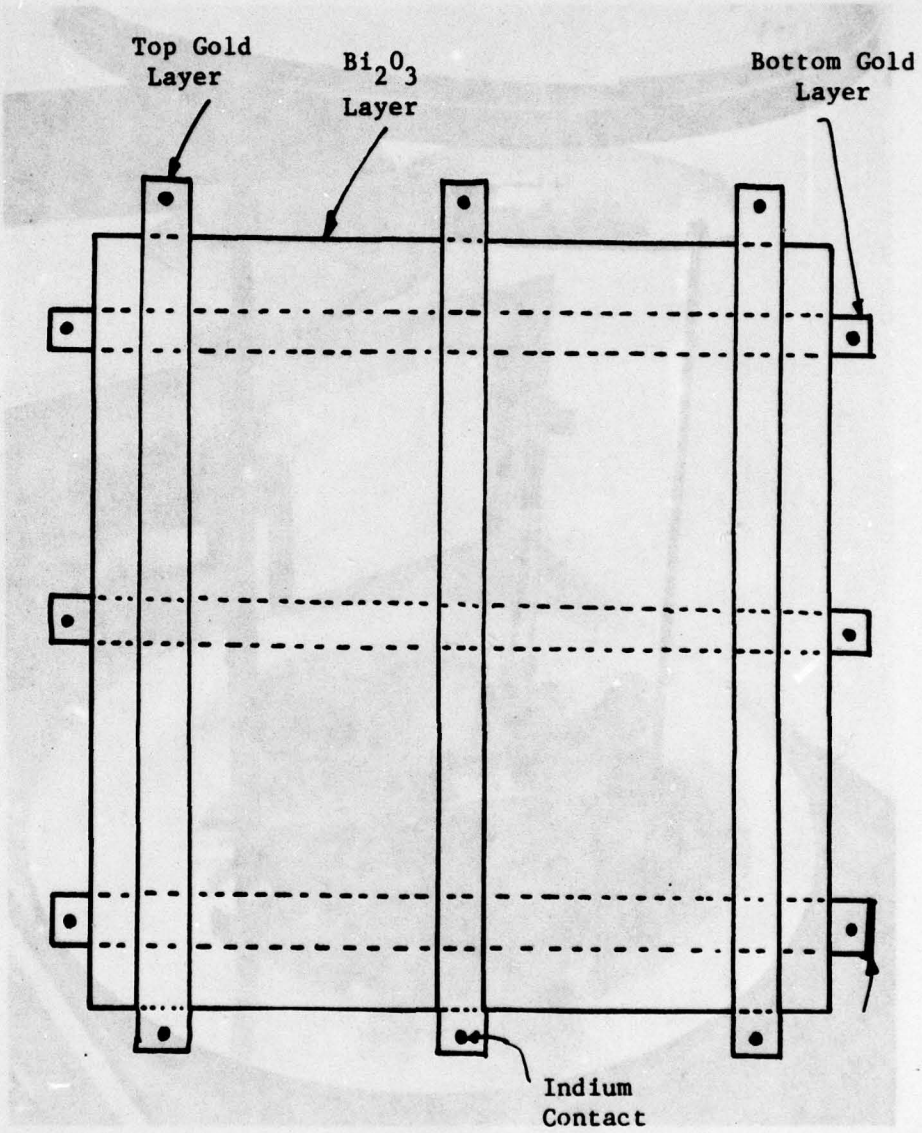


Figure 3

Top View of Completed Devices

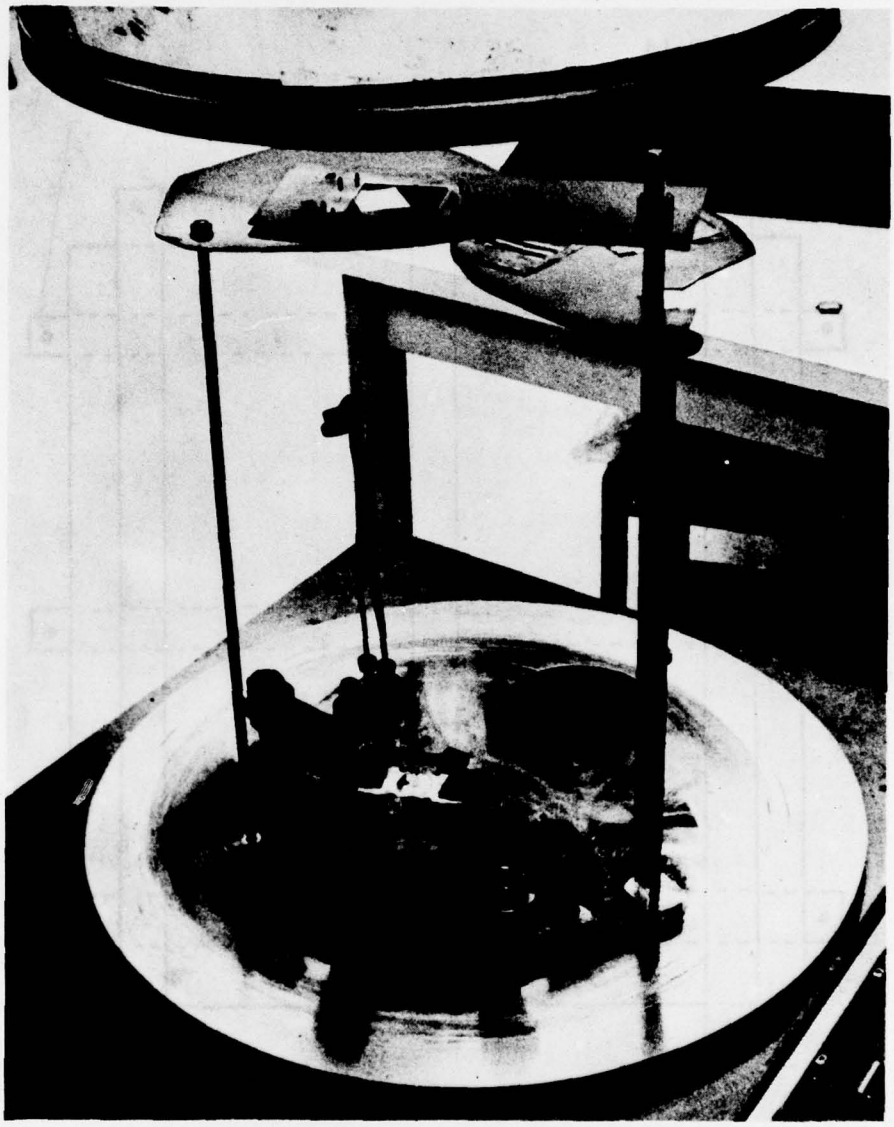


Figure 4

Vacuum Deposition Equipment
(Inside Bell Jar)

rotary-push feedthroughs. The substrate was placed in a holder above these masks. The source to substrate distance was 17 cm for the first twenty-four substrates and 40 cm for the other eleven. The reason for this change will be discussed in the results section of this report.

The evaporation equipment arrangement made it possible to fabricate nine Bi-O-Trons on one substrate under the same conditions without breaking the vacuum seal. In this way the amount of sample contamination was minimized.

The gold used for deposition was 99.999% pure. The bismuth trioxide powder used was 99% pure and had a monoclinic structure prior to melting.

The substrates used were pre-cleaned microscope slides that were 7.5 cm long and 5.0 cm wide. To improve film to substrate adhesion, each substrate was thoroughly cleaned before deposition. First, it was mechanically cleaned using the method outlined in Appendix II. Then the substrate was placed inside the vacuum bell jar and ionically cleaned. This was accomplished by bleeding in a small amount of air (pressure = 15μ) which was ionized by a small metal post that was raised to a potential of +1500v. Ion cleaning eliminated the adhesion problems previously encountered by other investigators.

Previous work has shown that film deposition rate is a critical parameter in making good amorphous Bi_2O_3 films.[1] Therefore, during the fabrication of Bi-O-Trons the rate of deposition and the film thickness were continually monitored by a crystal oscillator. The crystal used was an AT cut which oscillated at a frequency of about 4.42 MHz. The crystal mount was water-cooled because high crystal

temperatures can lead to inaccurate thickness measurements. Details of the film thickness monitoring system can be found in Appendix III.

Film devices were deposited at different rates and thicknesses, but all Bi_2O_3 films were deposited at a rate of at least 26 Å/sec. It was found that by using a larger amount of Bi_2O_3 in the boat than was actually needed to make the film, allowed the deposition rate to be more precisely controlled. Two grams was the amount used to deposit 5000Å of Bi_2O_3.

The time between the initial heating of the Bi_2O_3 and the time it is actually deposited on the substrate is known as warm-up time. This work has shown that this is also an important parameter in making good amorphous Bi_2O_3 films. This agrees with previous investigators.[1,4] For this reason, a standard warm-up procedure was followed. The current through the platinum boat was increased from 0 to 150 amperes in 30 ampere steps every 10 seconds. This resulted in an average warm-up time of 1.5 minutes.

A black dendritic material was found around the platinum boat. This is also in agreement with previous research.[1]

Electrical contacts could not be made directly to the gold film strips because they were so thin. Instead a small, conducting, relatively thick area was made on each gold strip and contact was made with it. A silver epoxy proved to be unsatisfactory. Excellent contacts were made by placing small indium spheres on the gold strips and then flattening them.

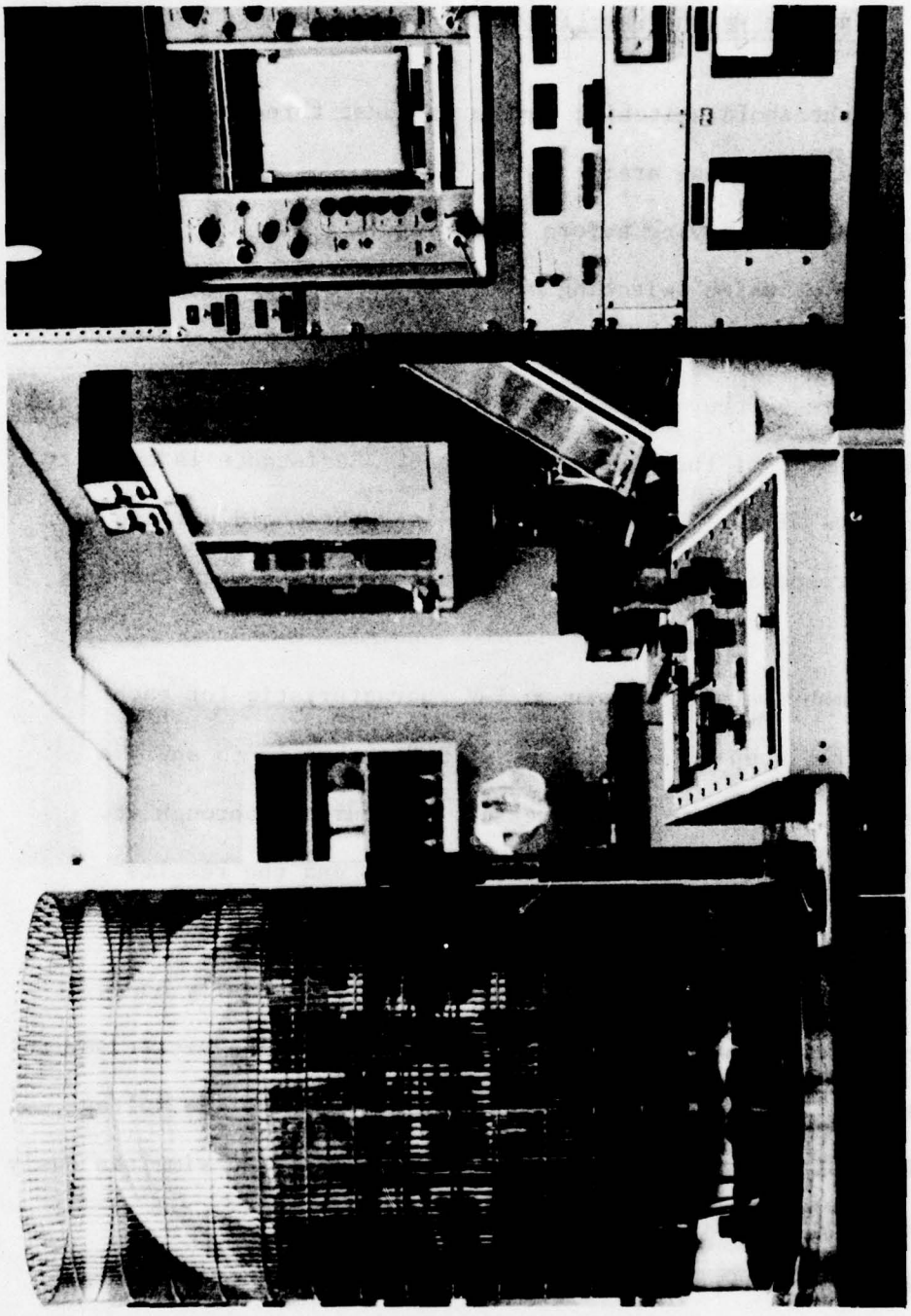


Figure 5
Vacuum Deposition and Monitoring Systems

SAMPLE MEASUREMENT APPARATUS AND TECHNIQUES

To test a threshold switching device at least three parameters need to be measured. These are:

1. resistance of device before switching (R_{off}).
2. voltage at which switching occurs ($V_{threshold}$).
3. resistance of device after switching (R_{on}).

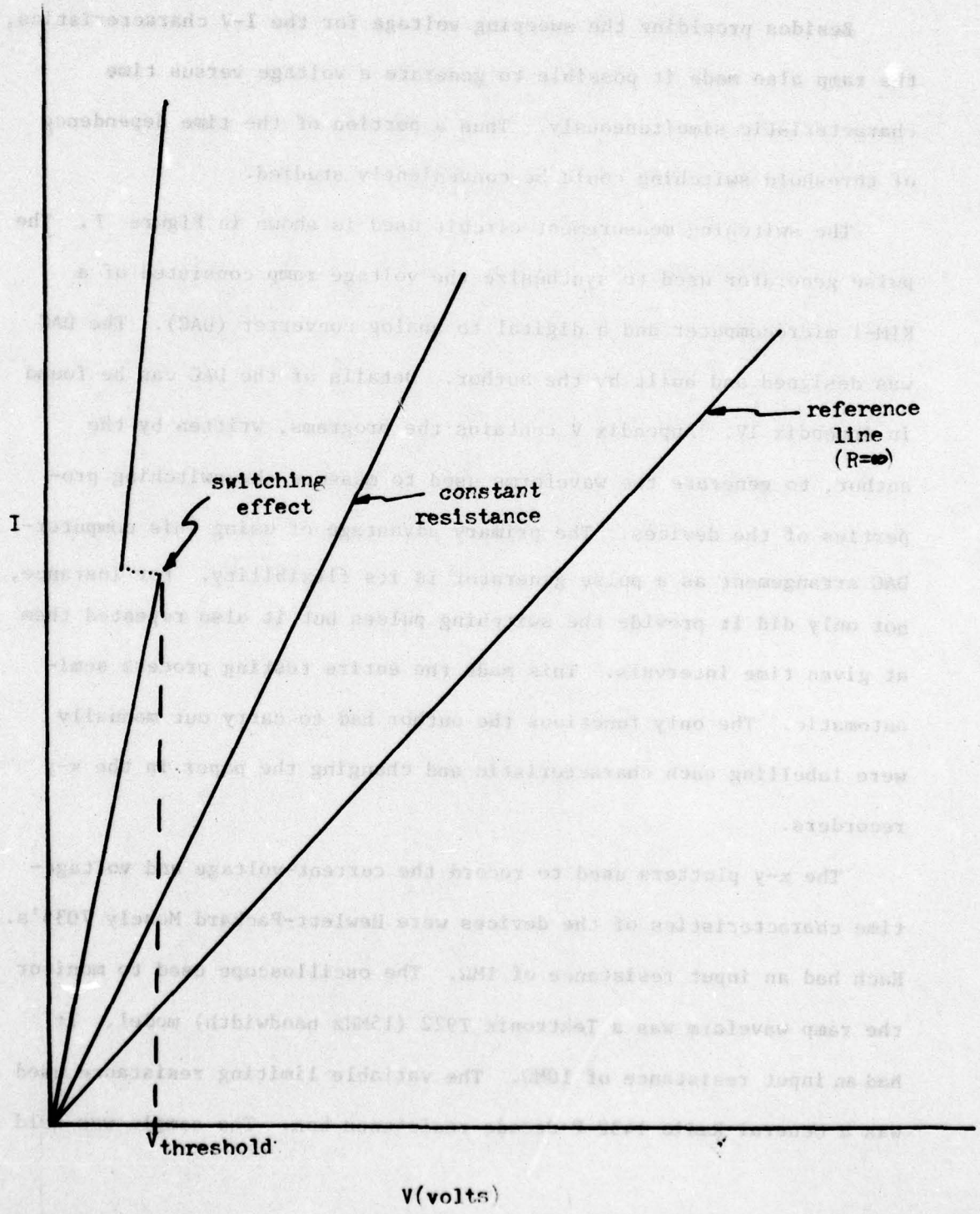
As shown in Figure 6, they are easily determined from a current-voltage (I-V) characteristic of the device under test. Resistance is equal to the inverse slope of the characteristic and the threshold voltage is the voltage corresponding to the discontinuity point between the R_{off} and R_{on} lines.

There are many ways to obtain an I-V characteristic for each device. The first step in a "point by point" method is to apply a given voltage across a device then measure the current through it. If this was repeated for many different voltages and the results graphed a complete current-voltage characteristic would result. Although this method requires little equipment and is easily done, it is too cumbersome and prone to errors to be practical. A better way to determine the current-voltage characteristic is to sweep the voltage values with a voltage waveform that changes with time and simultaneously monitor the current through the device.

Previous researchers used low frequency sinusoidal waveforms as the sweeping voltage.[1,5] For a sinusoidal waveform $\frac{dv}{dt} \alpha \sin(\omega t)$. By using a waveform with a time varying slope an unnecessary variable is introduced into the experiment. For this reason a better choice for

Figure 6

Typical Current-Voltage Characteristic of a Bi-O-Tron



a sweeping voltage waveform is a voltage ramp because $\frac{dv}{dt}$ = constant. The specific ramp used is shown in Appendix V. It rose to 6 volts in 4 seconds ($\frac{dv}{dt} = \frac{6 \text{ volts}}{4 \text{ sec}} = 1.5$ volts/sec).

Besides providing the sweeping voltage for the I-V characteristics, the ramp also made it possible to generate a voltage versus time characteristic simultaneously. Thus a portion of the time dependence of threshold switching could be conveniently studied.

The switching measurement circuit used is shown in Figure 7. The pulse generator used to synthesize the voltage ramp consisted of a KIM-1 microcomputer and a digital to analog converter (DAC). The DAC was designed and built by the author. Details of the DAC can be found in Appendix IV. Appendix V contains the programs, written by the author, to generate the waveforms used to measure the switching properties of the devices. The primary advantage of using this computer-DAC arrangement as a pulse generator is its flexibility. For instance, not only did it provide the switching pulses but it also repeated them at given time intervals. This made the entire testing process semi-automatic. The only functions the author had to carry out manually were labelling each characteristic and changing the paper in the x-y recorders.

The x-y plotters used to record the current-voltage and voltage-time characteristics of the devices were Hewlett-Packard Mosely 7035's. Each had an input resistance of 1MΩ. The oscilloscope used to monitor the ramp waveform was a Tektronix T922 (15MHz bandwidth) model. It had an input resistance of 10MΩ. The variable limiting resistance used was a General Radio 1432-P decade resistance box. The sample was held

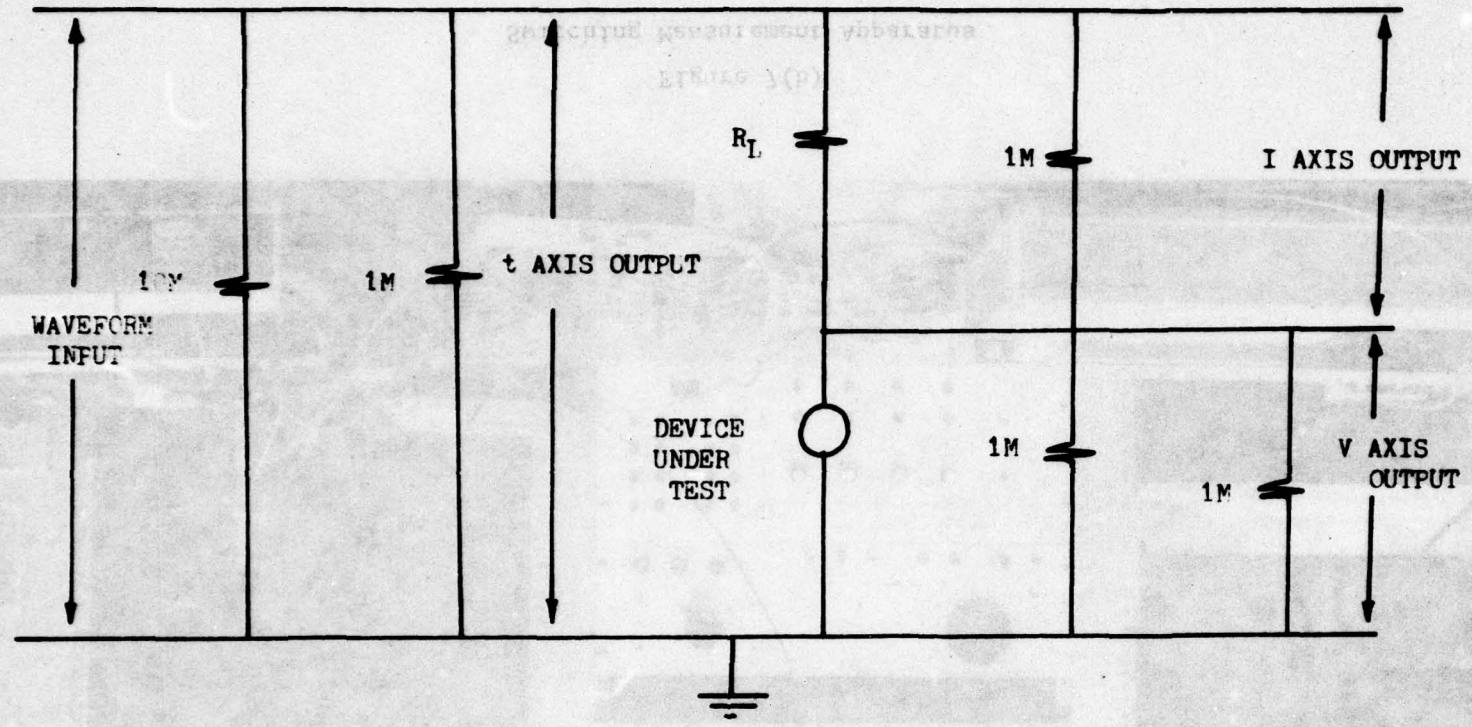


Figure 7(a)

Switching Measurement Circuit

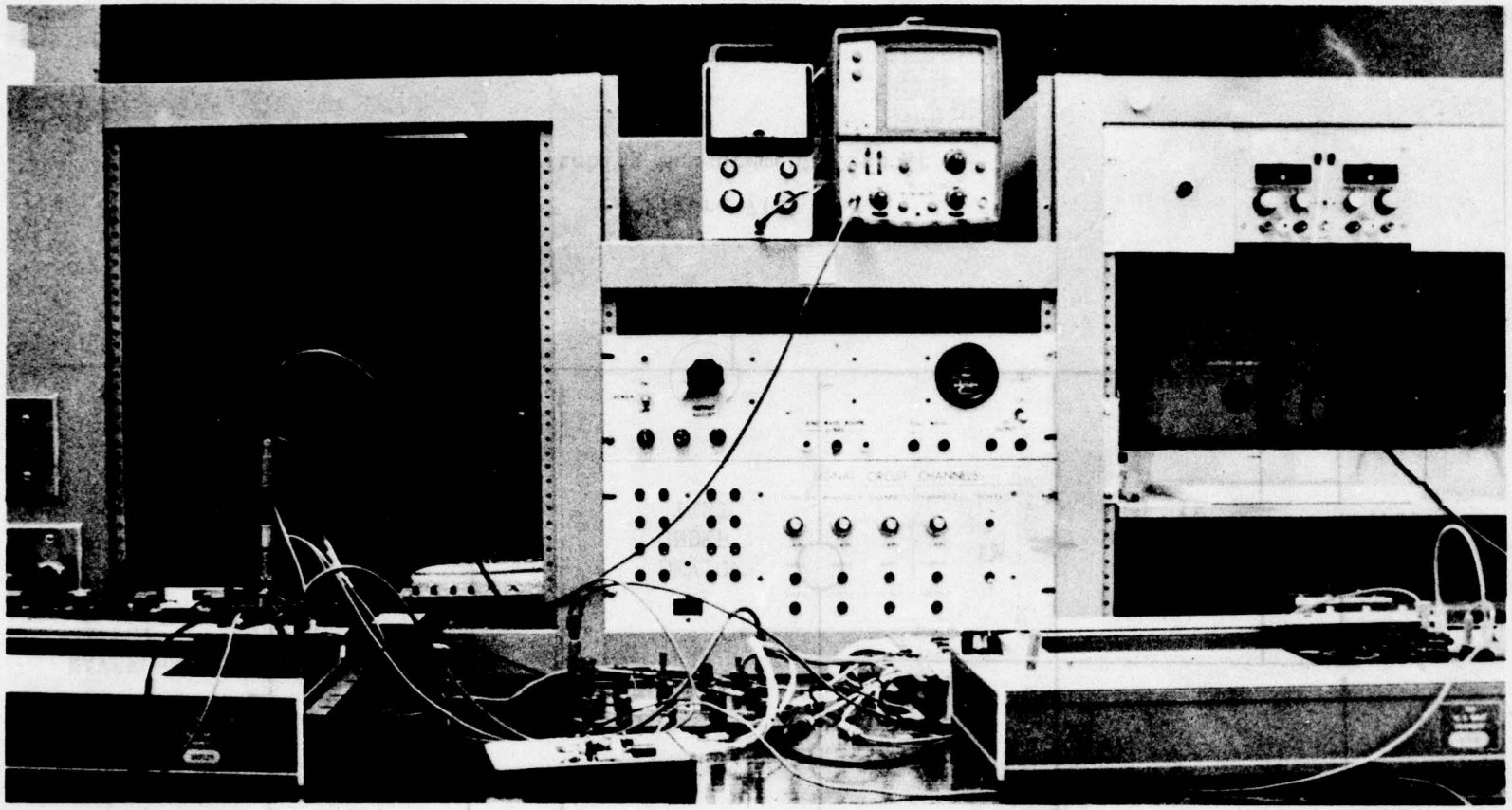


Figure 7(b)

Switching Measurement Apparatus

in a special holder which facilitated fast manipulation.

The entire arrangement was checked for proper operation between each device test by applying a switching pulse across the empty sample holder.

The resistances of films that did not display any switching characteristic were measured using a Heathkit IM-2518 vacuum tube voltmeter.

Some samples were studied with an Etek Autoscan U-1 scanning electron microscope. The samples investigated had to be specially prepared. Because an entire substrate would not fit onto the stage, the Bi-O-Trons to be studied had to be cut away from the substrate. This was done with a Dremel moto-tool and a glass cutting wheel. Then the Bi-O-Trons were mounted on aluminum pedestals and painted with conductive paint to reduce charge storage.

After preparation the specimen were studied with magnifications from 20x to 6000x. Photographs were taken with a polaroid camera attachment and Polaroid 52 film. Many stereoscopic photographs were taken by tilting the specimen.

RESULTS AND DISCUSSION

In this chapter results from all tests and observations are presented and discussed. The chapter is subdivided into four sections: general visual observations of the thin films, destructive testing, non-destructive testing and a summary of numerical results.

General Visual Observations

The Bi_2O_3 films made with a source to substrate distance of 17 cm were found to be optically darker than those made with the distance equal to 40 cm. This is because the darker ones had a higher free bismuth concentration. Also, the darker Bi_2O_3 films were observed to be much lighter (even clear) in the areas immediately to the gold strips. This suggests that the gold film has a strong affinity for free bismuth atoms and depletes the area surrounding it. This is in agreement with Holland's theory that the reason gold films adhere so well to bismuth trioxide is because of an oxygen deficiency in the film.[1,6]

Destructive Testing

When the voltage ramp waveform was applied to the optically dark films they were destroyed. This destruction was due to the joule heating associated with a relatively high current flowing through the device. This resulted in a silver-white filamentary growth around the edges of the Bi-O-Tron that was visible to the unaided eye. After the pulse was applied the resistance of the device was found to be on the order of 50Ω.

To determine the reason for this destruction some of the Bi-O-Trons were studied with an optical microscope and a scanning electron microscope (SEM). Figure 8 shows two of the photographs taken with the SEM.

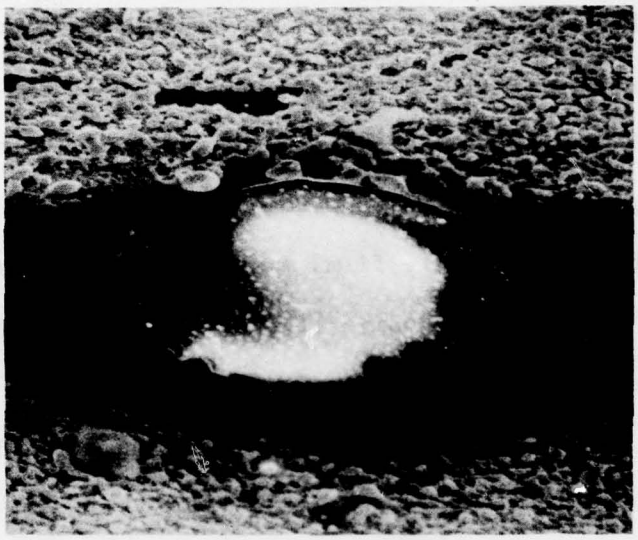
The holes shown in Figure 8 are on the order of 10 to 50 μm in diameter. To explain how the holes were formed and why the devices were destroyed the fabrication of the films must be investigated further.

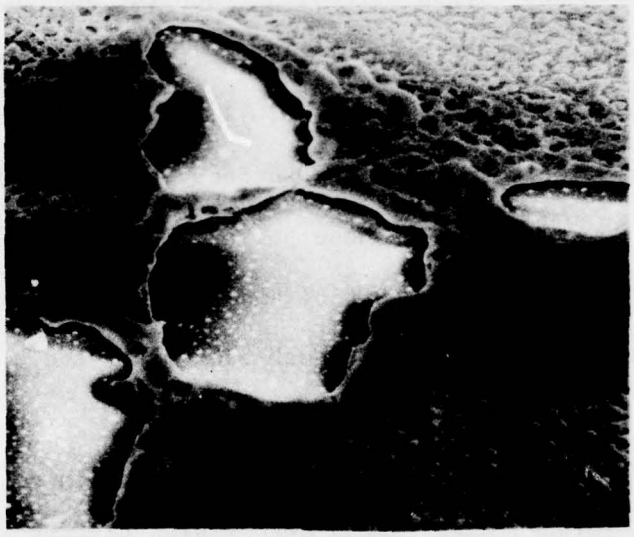
It has been shown thermodynamically,[7] by partial pressure measurements,[1] and by microprobe analysis[1] that Bi_2O_3 breaks down into its constituents (Bi and O_2) upon vaporization. The Bi and O_2 molecules then recombine to form the Bi_2O_3 film.

Consider the initial growth of an ideal Bi_2O_3 thin film. After evaporation, bismuth and oxygen molecules reach the substrate and begin to move about randomly [See Figure 9(a)]. If they do not meet another molecule they re-evaporate [See Figure 9(b)]. If they do meet another atom they are less likely to leave the surface and other molecules begin to migrate toward them.[8] These polyatomic "islands" become Bi_2O_3 when the proper proportions of Bi and O_2 are available. The islands continue to grow until they touch each other and a homogeneous film is formed.

This ideal process did not occur during the growth of the optically dark films. Some islands were formed with a high bismuth content. There are two possible explanations for this:

1. If bismuth atoms move significantly faster along the surface than oxygen molecules at high substrate temperatures then they would have a greater probability of finding another bismuth atom and not re-evaporating. This would result in an increased bismuth concentration



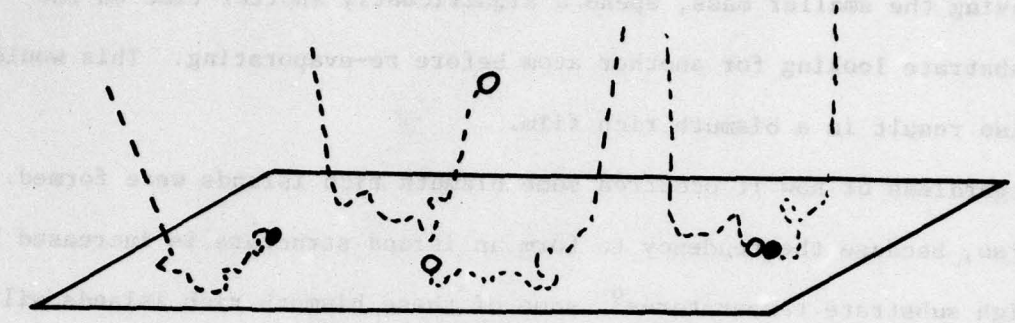


1000x

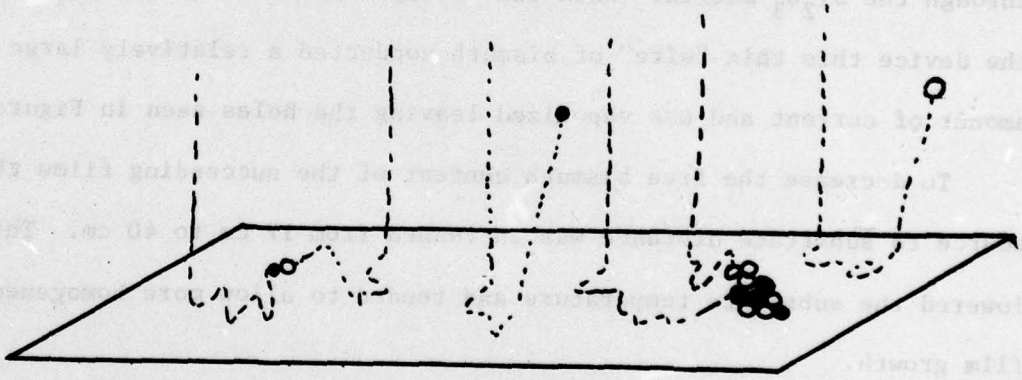
Bismuth Island Holes

Figure 8

The upper gold strip of this Bi-O-Tron was mechanically removed by forcing air across it. This allowed direct observation of the Bi_2O_3 layer.



(a)



(b)

● = Bismuth

O = Oxygen

Figure 9

Initial Film Growth (After Levine)

in the film, or

2. Because of the high substrate temperatures the oxygen molecules, having the smaller mass, spend a significantly shorter time on the substrate looking for another atom before re-evaporating. This would also result in a bismuth rich film.

Regardless of how it occurred some bismuth rich islands were formed. Also, because the tendency to form an island structure is increased by high substrate temperatures[9] some of these bismuth rich islands will exist as clusters of bismuth rich material in the finished film.

The holes in the Bi_2O_3 layer shown in Figure 8 were formed in the following way. One of the bismuth rich islands described above was large enough to make contact with both the bottom and top gold strips (See Figure 10). It provided a very low resistance, conducting path through the Bi_2O_3 matrix. When the voltage waveform was applied to the device this thin "wire" of bismuth conducted a relatively large amount of current and was vaporized leaving the holes seen in Figure 8.

To decrease the free bismuth content of the succeeding films the source to substrate distance was increased from 17 cm to 40 cm. This lowered the substrate temperature and tended to allow more homogeneous film growth.

The destroyed junctions also provided an excellent opportunity to study thermal filament growth because the joule heating created many filaments. It is thought that these filaments are thin, cylindrical areas of devitrified Bi_2O_3. That is, within these filaments the Bi_2O_3 possesses a long range order unlike the matrix around it which only has short range order.

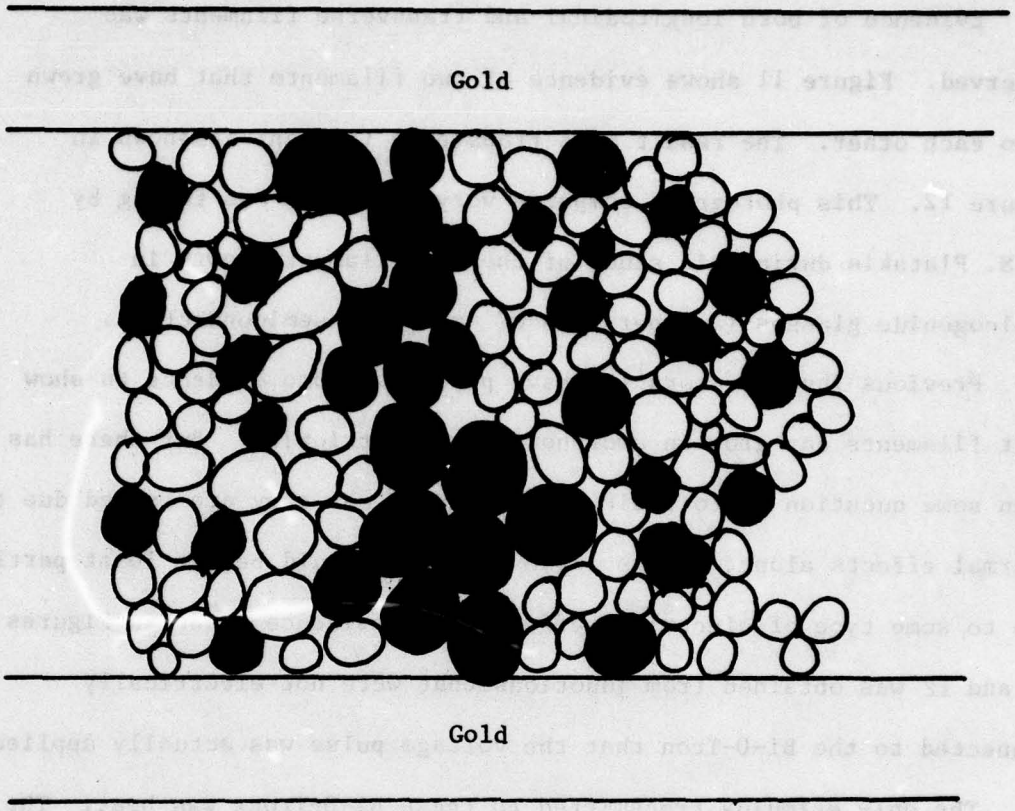


Figure 10

A Bismuth Island Conducting Path

Evidence of both longitudinal and transverse filaments was observed. Figure 11 shows evidence of two filaments that have grown into each other. The result of a transverse filament is shown in Figure 12. This photograph compares very well with one taking by N. S. Platakis during his study of thermal filament growth in chalcogenide glasses (another type of amorphous semiconductor).

Previous investigators[1,5] have presented some evidence to show that filaments can grow in amorphous bismuth trioxide. But there has been some question as to their origin. Some say they are formed due to thermal effects alone, others argue that they could be, at least partly, due to some type of electrical effect. The evidence shown in Figures 11 and 12 was obtained from junctions that were not electrically connected to the Bi-O-Tron that the voltage pulse was actually applied to. The only stimulus transmitted to these Bi-O-Trons was heat. The existence of the filaments in these electrically isolated regions shows that both transverse and longitudinal filaments can be created due to thermal effects alone. This does not necessarily imply that filaments due to electrical or electro-thermal effects are not conceivable, it simply affirms that purely thermal filaments are possible.

Non-Destructive Testing

Most films fabricated with the increased source to substrate distance exhibited some type of switching effect. The ones that did not, all had resistances of approximately 50Ω.

Consider a typical switching measurement test. The voltage was increased to a certain point where switching occurred. After switching the voltage increased but at a slower rate because of its new lower

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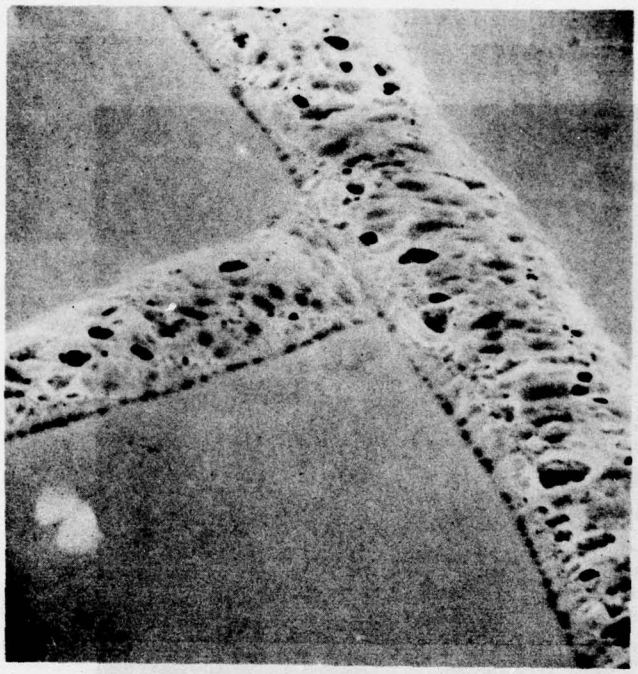

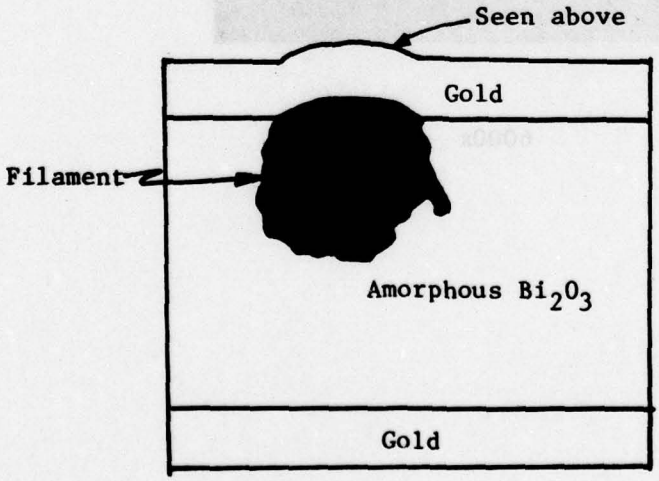

Figure 11
Longitudinal Thermal Filaments

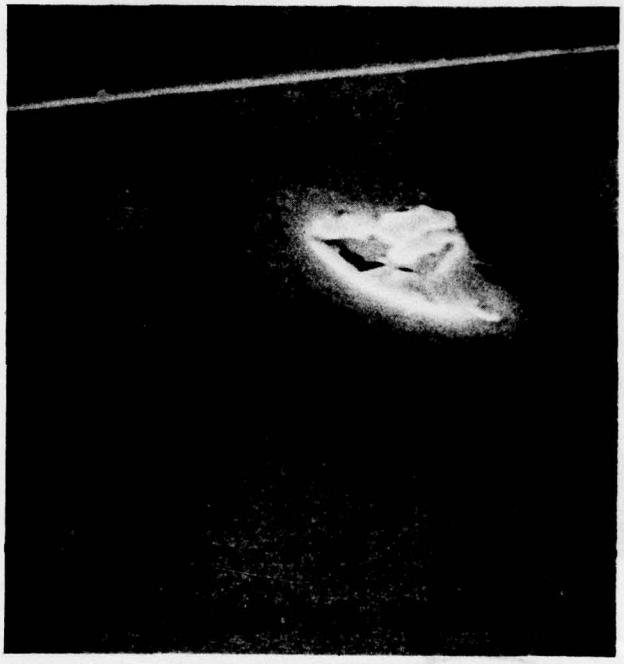

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Figure 12
Transverse Thermal Filament Depression

resistance until the applied voltage ramp was turned off. At this point the voltage across the device decreased very quickly to a point and then decreased slowly to zero voltage. This latter behavior indicates that some type of charge storage had occurred in the Bi-O-Tron.

It was found that the voltage at which switching occurred, known as the threshold voltage, was highest the first time the voltage ramp was applied and decreased for each repetition thereafter until it stabilized at a very low voltage (~ 0.1 volts). This suggests that some type of electronic mechanism is associated with threshold switching.

Because the Bi_2O_3 films were fabricated by the direct vacuum deposition process with the source directly beneath the substrate, the Bi-O-Tron in the center position on the substrate will have the thickest Bi_2O_3 region. It was found that a higher threshold voltage was necessary to switch the center junction than to switch any of the others. This preliminary work shows that the threshold voltage increases with increasing film thickness. This suggests that the threshold mechanism may be related to the electric field.[1]

As mentioned previously, after many repetitions (5 to 15) a stable, high conductivity state was reached. To investigate this state, the polarity of the voltage ramp was reversed.

Figure 13 shows both the I-V characteristic of the stable state before polarity reversal and the ones immediately after it. This suggests that this stable state could be due to conduction by an electro-thermal filament.

In contrast, Figure 14 suggests that another stable state was due

Figure 13

Current-Voltage Characteristics of Bi-O-Tron #29-D

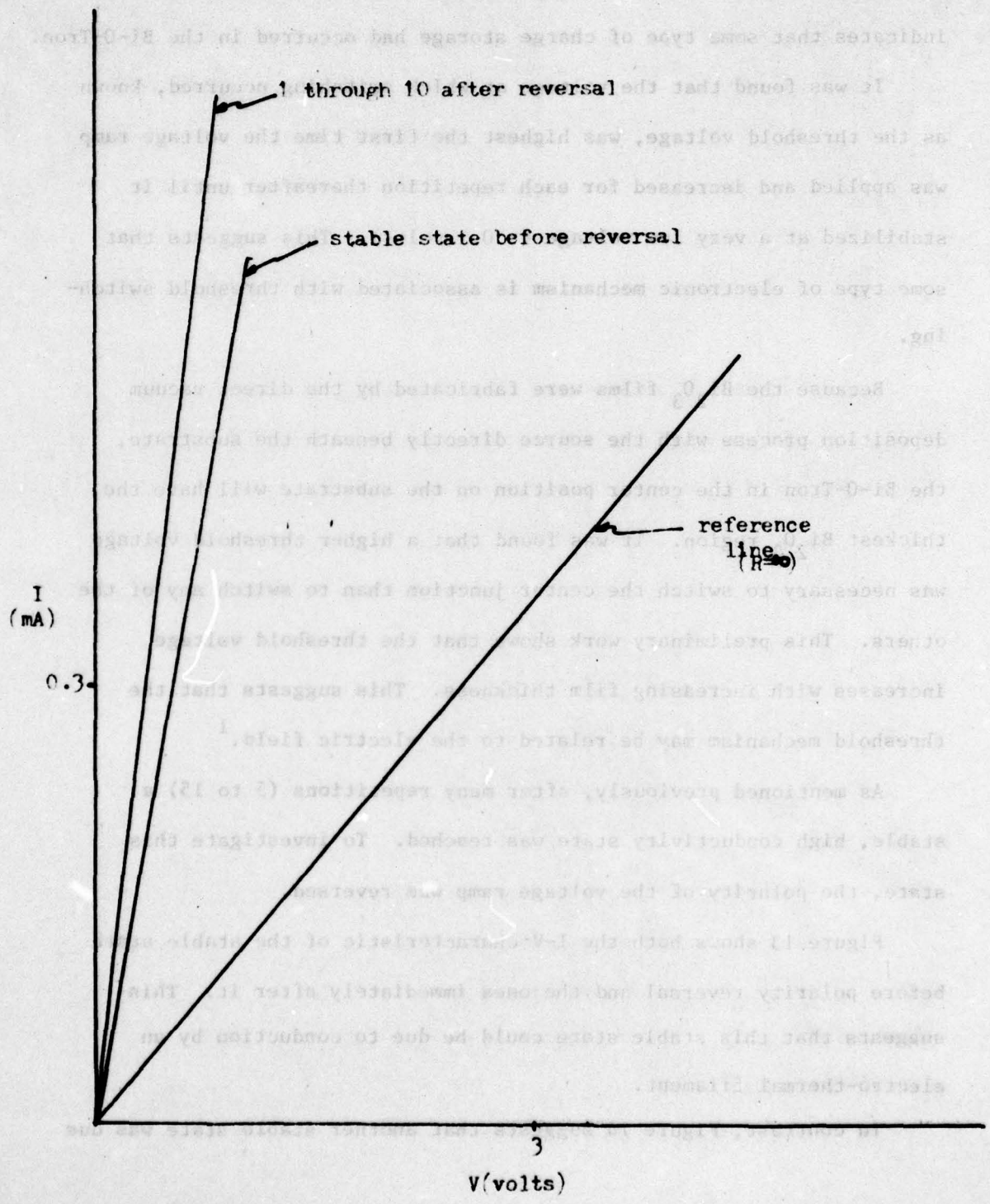
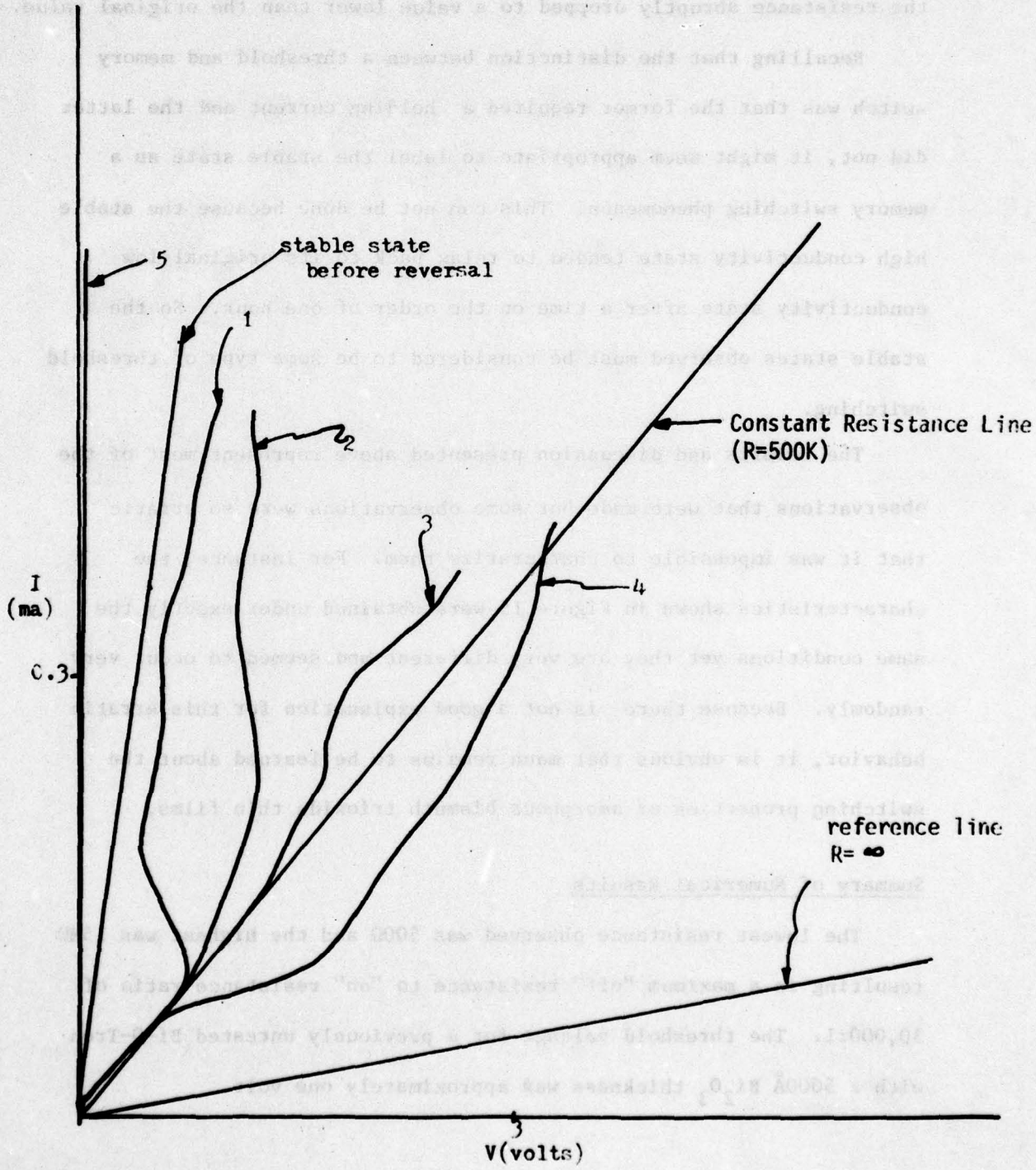


Figure 14

Current Voltage Characteristics of Bi-O-Tron #29-E



to some type of electronic conduction mechanism. It shows that after the voltage was first reversed the resistance increased and then continued to increase until the fifth repetition of voltage ramp when the resistance abruptly dropped to a value lower than the original value.

Recalling that the distinction between a threshold and memory switch was that the former required a holding current and the latter did not, it might seem appropriate to label the stable state as a memory switching phenomenon. This can not be done because the stable high conductivity state tended to relax back to its original low conductivity state after a time on the order of one hour. So the stable states observed must be considered to be some type of threshold switching.

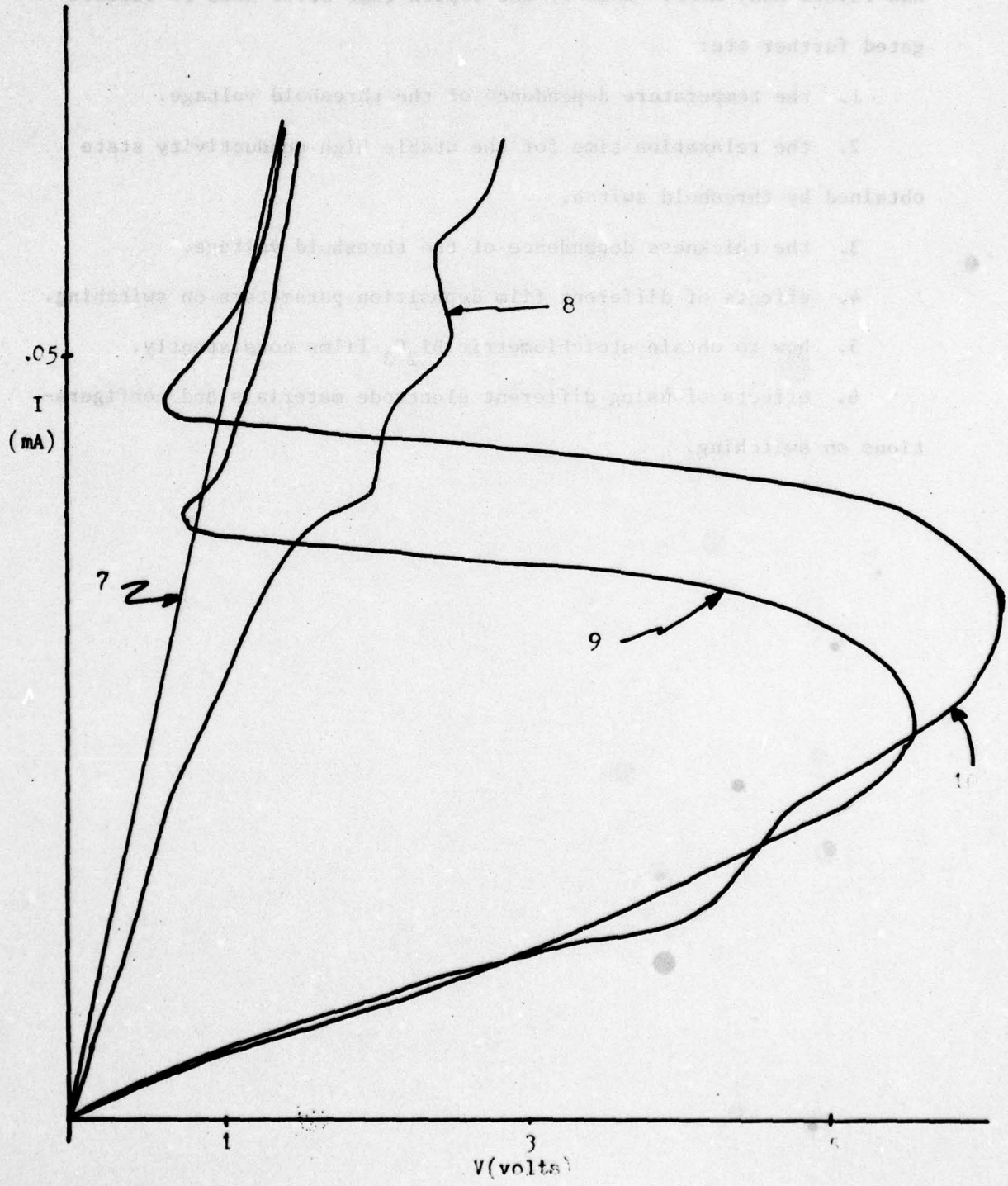
The results and discussion presented above represent most of the observations that were made but some observations were so erratic that it was impossible to characterize them. For instance, the characteristics shown in Figure 15 were obtained under exactly the same conditions yet they are very different and seemed to occur very randomly. Because there is not a good explanation for this erratic behavior, it is obvious that much remains to be learned about the switching properties of amorphous bismuth trioxide thin films.

Summary of Numerical Results

The lowest resistance observed was 500Ω and the highest was 15MΩ resulting in a maximum "off" resistance to "on" resistance ratio of 30,000:1. The threshold voltage for a previously untested Bi-O-Tron with a 5000Å Bi_2O_3 thickness was approximately one volt.

Figure 15

Current-Voltage Characteristics of Bi-O-Tron #29-A



SUGGESTIONS FOR FURTHER INVESTIGATION

Like most research, this project has answered a few questions but has raised many more. Some of the topics that still need to investigated further are:

1. the temperature dependence of the threshold voltage.
2. the relaxation time for the stable high conductivity state obtained by threshold switch.
3. the thickness dependence of the threshold voltage.
4. effects of different film deposition parameters on switching.
5. how to obtain stoichiometric Bi_2O_3 films consistently.
6. effects of using different electrode materials and configurations on switching.

CONCLUSIONS

The principal conclusions of this research are:

1. Direct vacuum deposition is a good way to fabricate Bi-O-Trons. But the process must be carefully controlled to obtain a stoichiometric bismuth trioxide layer. A device that has a high free bismuth concentration will not exhibit any switching characteristics.

2. At least some filamentary growth in amorphous bismuth trioxide thin films can be explained by an exclusively thermal model.

3. Threshold switching can not be explained by an exclusively thermal or exclusively electronic model. Instead both of these effects must be included. That is, threshold switching is due to some type of electro-thermal mechanism.

4. The switching characteristics of Bi-O-Trons are much too erratic and unreliable to be used as memory cells at the present time.

5. There is still much to be learned about amorphous semiconductors and their switching properties. A complete explanation of the results presented in this report and others similar will greatly increase the present understanding of solids in general.

Acknowledgements

I would like to thank my advisor, Professor Ralph P. Santoro, for the insight, inspiration and ideas he provided, and also for allowing me to make my own mistakes and then correct them myself. Without his help this project would not have been possible. And because of his style, I have learned much about the subject and myself.

Dr. J. H. Halford initially encouraged me to pursue this project, provided me with some important information and equipment and has been a helpful "long-distance" advisor; for his help I am sincerely grateful.

I would also like to thank the following people who helped me at various stages of the project. Mr. Jack Moore and Midshipman Sam Perez assisted with their excellent photography work. Mr. Carl Owen helped by machining some new pieces of equipment for the vacuum deposition system. Mr. Willi Umlaudt taught me how to use the scanning electron microscope and also assisted in making surface micrographs. Dr. J. J. Fontanella allowed me to use his polishing equipment and taught me how to grind a bell jar. And Miss Cindy Polacek for her patience and the typing of this report.

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Appendices

APPENDIX I

Basic Mask Fabrication Process

- suggested by Dr. J. H. Halford

A. Making a Negative of the Mask Pattern

1. Construct a black and white enlargement of the pattern desired.
2. Set up a photocopier for reduction.
3. Photograph the poster pattern with Kodalith on the Type 3 sheet film - make two negatives of each pattern.
4. Develop the negative in a darkened room.

B. Making the Stainless Steel Mask

1. Scrub the stainless steel mask with an abrasive.
2. Rinse the mask thoroughly with distilled water.
3. Stir the mask in a 20% solution of H_3PO_4.
4. Repeat step B. 2.
5. Bake the mask in a oven, @ about 400°F.

C. Sensitizing the Mask - must be done in darkened room

1. Dip the mask in some kodak photo resist.
2. Place mask in a spinner and spin for about ten minutes.
3. Turn on heat in spinner and spin for 15 more minutes.

Note: This step should probably be repeated at least once.

D. Exposing the Sensitized Masks

1. Tape two aligned negatives of the pattern together at one end.
2. Insert the sensitized stainless steel sheets between the negatives and put this inside two glass plates.

3. Expose both sides of the mask with two 375 W flood lights.

E. Developing the Exposed Masks

1. Agitate the mask in some KPR developer in a dark room.

2. Rinse the mask thoroughly with distilled water.

3. Bake the mask for ten to fifteen minutes at ~ 400°F.

4. Etch the mask in a hydrochloric acid solution (3 parts water to one part acid).

5. Rinse mask in water, then dip in concentrated sulfur acid to remove any extra KPR.

6. Mask is ready to be mounted on a thicker stainless plate.

Note: Masks were .002" thick.

APPENDIX II

Mechanical Substrate Cleaning Method

1. Put substrates in stainless steel holder.
2. Put stainless steel holder in ultrasonic tank filled with distilled water and alconox. Make sure not to touch bottom of tank with holder - this leads to contamination of the tank itself.
3. Rinse substrates thoroughly with distilled water.
4. Rinse again by putting holder back - ultrasonic cleaner with distilled water in the tank.
5. Dry substrates in an oven at about 100°C.
6. Store clean substrates in a dessicant jar.

APPENDIX III

Thin Film Thickness Monitoring System

The equipment used was a Kronos QM-331 film thickness monitor with a RO-200 and a RI-100 rate/thickness accessory.

This equipment uses the principles of period measurement to determine film thicknesses. This is a linear measurement because an AT cut quartz crystal is characterized by the equation,

$$\tau = KT$$

where τ = period of oscillation

K = constant of proportionality

T = thickness.

So for any changes in thicknesses,

$$\Delta\tau = K\Delta T.$$

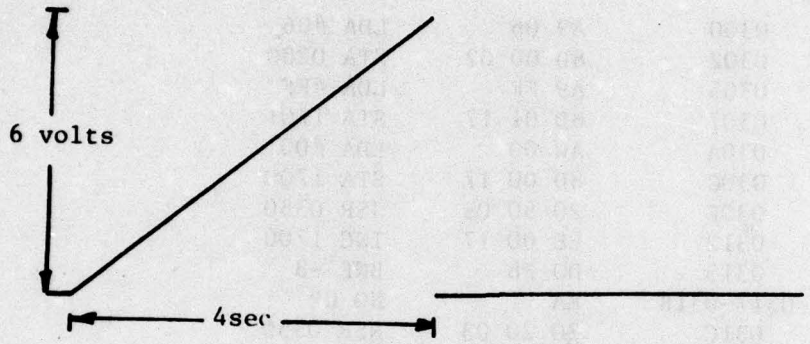
Therefore by measuring the period of the crystal oscillators, the thickness of the film deposited can be readily determined.

APPENDIX IV

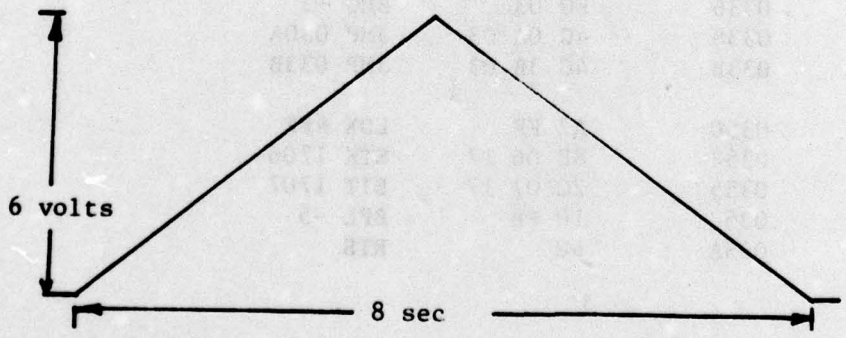
1. Multi-Shot Ramp Program - generates the waveform shown below a given number of times.

```
0000    A9 FF       LDA #FF
0002    8D Ø1 17    STA 1701
0005    A9 ØØ       LDA #00
0007    8D ØØ 17    STA 1700
000A    A2 FF       LDX #FF
000C    8E Ø6 17    STX 1706
000F    2C Ø7 17    BIT 1707
0012    10 FB       BPL -5
0014    EE ØØ 17    INC 1700
0017    DØ F1       BNE -15
0019    AØ E7       LDY #E7
001B    A2 FF       LDX #FF
001D    8E Ø7 17    STX 1707
0020    2C Ø7 17    BIT 1707
0023    1Ø FB       BPL -5
0025    88          DEY
0026    DØ F5       BNE -11
0028    CE ØØ Ø2    DEC 0200
002B    FØ Ø3       BEQ +3
002D    4C Ø5 ØØ    JMP 0005
0030    4C 3Ø ØØ    JMP 0030
0033    A9 Ø6       LDA #06
0035    8D ØØ Ø2    STA 0200
0038    4C ØØ ØØ    JMP 0000
```

Note: 0200 contains number of repetitions to be performed.



Ramp Waveform



Triangular Waveform

2. Triangle Waveform Program

- output shown above.

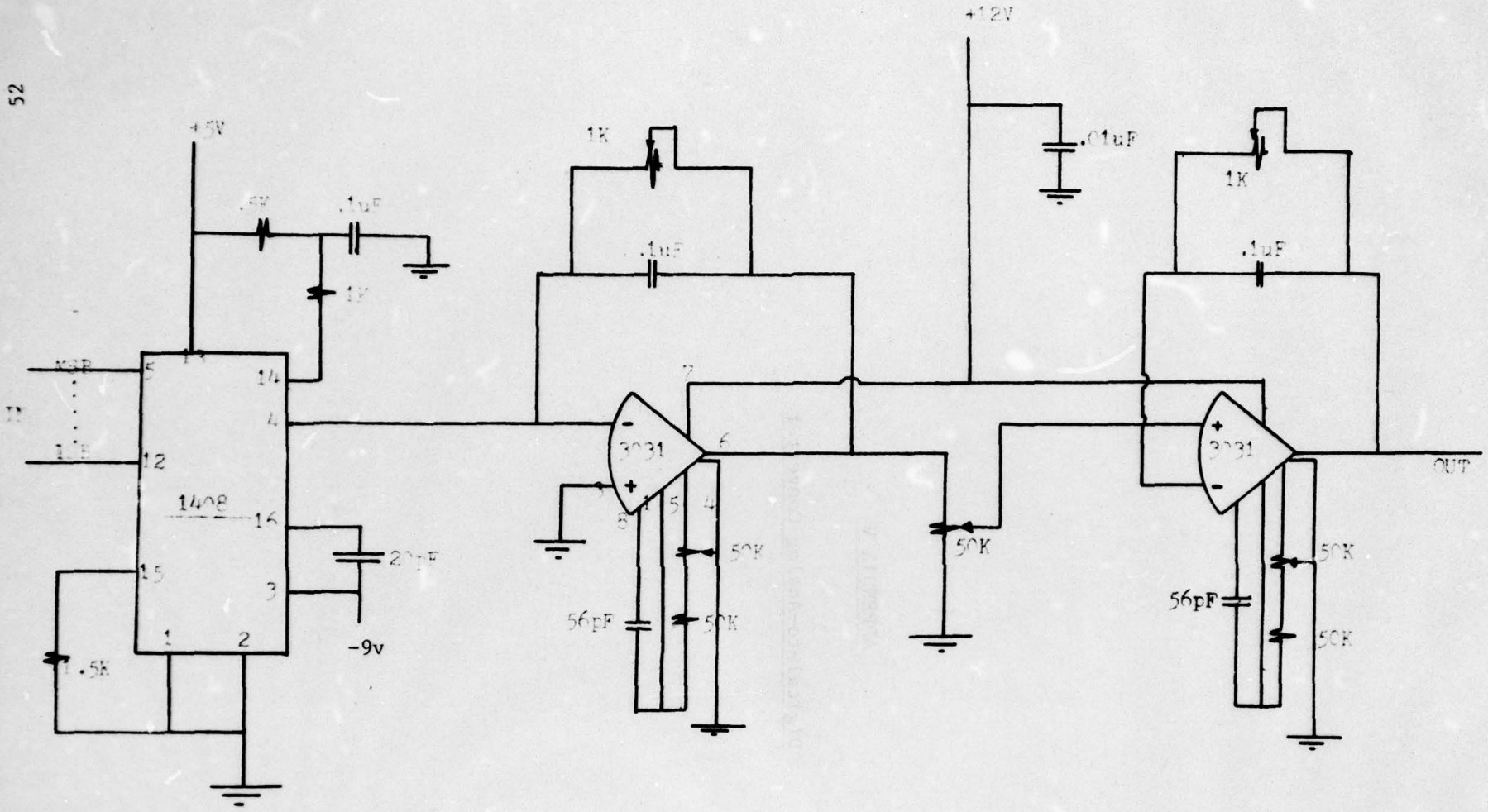
- can be repeated a given number of times.

```
0300        A9 06       LDA #06
0302        8D 00 02    STA 0200
0305        A9 FF       LDA #FF
0307        8D 01 17    STA 1701
030A        A0 00       LDA #00
030C        8D 00 17    STA 1700
030F        20 50 03    JSR 0350
0312        EE 00 17    INC 1700
0315        D0 F8       BNE -8
0317-031B   EA          NO OP
031C        20 20 03    NSR 0350
031F        CE 00 17    DEC 1700
0322        D0 F8       BNE -8
0324        A0 73       LDY #73
0326        A2 FF       LDX #FF
0328        8E 07 17    STX 1707
032B        2C 07 17    BIT 1707
032E        10 FB       BPL -5
0330        88          DEY
0331        D0 F5       BNE -11
0333        CE 00 02    DEC 0200
0336        F0 03       BEQ +3
0338        4C 0A 03    JMP 030A
033B        4C 3B 03    JMP 033B

0350        A2 FF       LDX #FF
0352        8E 06 17    STX 1706
0355        2C 07 17    BIT 1707
0358        10 FB       BPL -5
035A        60          RTS
```

APPENDIX V

Digital-to-Analog Converter



Digital-to-Analog Converter

APPENDIX VI

Specifications of Equipment and Materials

Materials for device:

1. Bismuth Trioxide - 99% pure

   Supplier: Matheson, Coleman and Bell

2. Gold - 99.999+% pure

   Supplier: American Smelting and Refining (Globe Plant)

3. Substrates - precleaned microscope slides

   Supplier: Fisher Scientific

Equipment used to fabricate devices:

1. Vacuum System - Varian VE-20 with Bayard-Alpert Gauge

2. Film Thickness Monitoring System - Kronos QM-331 with RO-200 rate/thickness printed circuit board and RI-100 deposition rate indicator.

   Crystals used were: Kronos XT-5544 (4.42MHz)

3. Recorder of film thickness and rate - Hewlett-Packard 322 Dual Channel Recorder.

4. Stainless Steel Shim Stock for Masks - .002" thick

   Supplier: Ullbrich Stainless Steels and Specialty Metals

Switching measurement equipment:

1. x-y Recorders - Hewlett-Packard Mosely 7035

2. Oscilloscope - Tektronix T922 (15MHz)

3. Vacuum Tube Voltmeter - Heathkit IM-5218

4. Decade Resistor Box - General Radio 1432-P

5. Microcomputer - KIM-1

6. Digital/Analog Converter - See Appendix V

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Amorphous semiconductors.
Bismuth oxide.
Thin films.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This project involves the design, development, and fabrication of a read-mostly memory using bistable, amorphous bismuth trioxide thin films as the memory cell material. Many gold-amorphous bismuth trioxide-gold layered devices, known as Bi-O-Trons were fabricated, and their switching properties were investigated. The Bi-O-Trons were made by way of direct vacuum deposition. A unique microprocessor controlled measurement method was developed. This report also contains evidence that filaments can be formed by OVER !!

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exclusively thermal effect. Also, evidence that suggests an electro-thermal model of threshold switching is presented and discussed. Finally a conclusion about the possibility of the immediate application of Bi-O-Trons as memory cells is presented.

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